

AD-A176 283

HISTORY OF SOLID STATE BATTERIES(U) MINNESOTA UNIV  
MINNEAPOLIS CORROSION RESEARCH CENTER B B OWENS ET AL.  
JAN 87 ONR-TR-5 N00014-85-K-0634

1/1

UNCLASSIFIED

F/G 10/3

NL





1.0



2.8



2.5



5.0



3.15



2.2



1.1



3.5



2.0



4.0



1.8



1.25



1.4



1.6

12

AD-A176 283

OFFICE OF NAVAL RESEARCH

Contract N00014-85-K-0634

R & T Code 413d019---01  
Replaces Old  
Task # 627-850

TECHNICAL REPORT NO. 5

History of Solid State Batteries

by

Boone B. Owens and M. Z. A. Munshi  
Department of Chemical Engineering and Materials Science  
University of Minnesota  
Minneapolis, MN 55455

Prepared for

Symposium on Battery History

171st Meeting of The Electrochemical Society

Philadelphia, PA  
May, 1987

DTIC  
EXECTE  
JAN 29 1987  
AP

Reproduction in whole or in part is permitted for any  
purpose of the United States Government

This document has been approved for public release  
and sale; its distribution is unlimited

DTIC FILE COPY

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION <b>Unclassified</b>		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT <b>Unclassified/Unlimited</b>	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE		4. PERFORMING ORGANIZATION REPORT NUMBER(S) <b>ONR Technical Report #5</b>	
6a. NAME OF PERFORMING ORGANIZATION <b>Corrosion Research Center</b>		6b. OFFICE SYMBOL (If applicable)	
6c. ADDRESS (City, State, and ZIP Code) <b>University of Minnesota Minneapolis, MN 55455</b>		7a. NAME OF MONITORING ORGANIZATION <b>Office of Naval Research, Resident Rep.</b>	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION <b>Office of Naval Research</b>		8b. OFFICE SYMBOL (If applicable) <b>Code 1113</b>	
8c. ADDRESS (City, State, and ZIP Code) <b>800 North Quincy Street Arlington, VA 22217-5000</b>		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER <b>Contract No. N00014-85-K-0634</b>	
11. TITLE (Include Security Classification) <b>History of Solid State Batteries</b>		10. SOURCE OF FUNDING NUMBERS	
12. PERSONAL AUTHOR(S) <b>Boone B. Owens and M.Z.A. Munshi</b>		PROGRAM ELEMENT NO.	PROJECT NO.
13a. TYPE OF REPORT <b>Technical</b>	13b. TIME COVERED FROM <b>7/15/85</b> TO <b>12/30/86</b>	TASK NO.	WORK UNIT ACCESSION NO.
14. DATE OF REPORT (Year, Month, Day) <b>January 1987</b>		15. PAGE COUNT <b>4 pages</b>	
16. SUPPLEMENTARY NOTATION <b>To be presented in the symposium "Battery History" at the 171st National Meeting of the Electrochemical Society, May 1987.</b>			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		battery, solid state electrolyte, solid state battery	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>Historically, batteries have combined liquid electrolytes with solid electrodes because solid electrolytes were too resistive and could not accommodate the volumetric changes associated with the cell reactions. Solid materials utilized as battery electrolytes include: (1) simple ionic salts - <math>\text{AgI}</math>; (2) double salt compounds - <math>\text{RbAg}_4\text{I}_5</math>; (3) dispersed phase solid electrolytes - <math>\text{KII}(\text{Al})_3</math>; (4) ceramic compounds - <math>\text{Na}-\text{g}^{\text{th}}-\text{Al}_2)_3</math>; (5) in-situ formed electrolytes - <math>\text{LiI}</math>; (6) glasses - <math>\text{LiI}-\text{Li}_2\text{S}-\text{P}_2\text{S}_5</math>; (7) polymer electrolytes - <math>(\text{PEO})_8\text{LiClO}_4</math>. Commercialization has been limited because of performance and cost factors.</p>			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION <b>Unclassified</b>	
22a. NAME OF RESPONSIBLE INDIVIDUAL <b>Boone B. Owens</b>		22b. TELEPHONE (Include Area Code) <b>(612) 625-1332</b>	22c. OFFICE SYMBOL

## HISTORY OF SOLID STATE BATTERIES

Boone B. Owens and M. Z. A. Munshi

Department of Chemical Engineering  
and Materials Science  
Corrosion Research Center  
University of Minnesota, Minneapolis, MN 55455

Solid electrolytes have been of considerable interest because of the possibility for fabricating batteries that would exhibit enhanced stability and operate over a wide temperature range. The scientific activity devoted to this field has been a function of the availability of solid electrolyte materials. Prior to 1965 there were limited materials that exhibited ionic conductivities of sufficient magnitude for a practical battery (1,2). Whereas liquid electrolytes exhibited conductivities of nominally one S/cm solid electrolytes exhibited conductivities of less than  $10^{-6}$  S/cm. It was known that certain solid electrolytes exhibited "liquid like" conductivity values of one S/cm at elevated temperatures. The high temperature phases of the silver halides and some cuprous halides exhibited this characteristic. However, at ambient temperatures, the stable crystal structures exhibit very limited ionic mobility.

Early investigators of solid state batteries developed several electrochemical systems for low power ordinance applications during the late 1950s, as shown in Table 1 (3,4). These cells had very high internal resistances and were limited to current densities of a few microamps/cm<sup>2</sup>. Since most of these cells were based on silver ion conducting electrolytes it was necessary to use silver as the anode; therefore the cell voltages and the energy densities were quite low. Nonetheless, these batteries did exhibit long shelf-life and good mechanical stability.

The major limitations of low specific energy and power were due to the solid state of the electrolyte material. Consequently, battery scientists interested in improved solid state batteries had to develop more conductive solid electrolyte elements. This could be achieved by finding new structures in which the ionic transport occurred more readily, or by developing techniques for fabricating the electrolyte in a very thin configuration with high surface area. Both of these approaches were followed during the subsequent twenty years. The discovery of highly conducting double salts of silver compounds led to the development of solid state cells in which the internal resistance was proportionately reduced. Ag<sub>3</sub>SI had an ionic conductivity of 0.01 S/cm at ambient temperature and RbAg<sub>4</sub>I<sub>5</sub> had a value of 0.27 S/cm. These salts were combined with silver anodes and the resulting cells were capable of current drains in excess of 100 mA/cm<sup>2</sup>.

The use of polyiodide cathodes resulted in cells, of the types Ag/RbAg<sub>4</sub>I<sub>5</sub>/Me<sub>4</sub>NI<sub>3</sub> capable of efficient discharge over a wide temperature range. Because of the absence of phase transitions stable performance was observed between -40 and +70°C. Further, these solid state cells could be stored as active primary cells for over 10 years (5). Although the system performed relatively efficiently, inherent limitations of cost and energy content restricted their application. Nonetheless, it did illustrate the feasibility of totally solid-state batteries that could accommodate the volume changes associated with cell discharge reaction and give efficient performance over an extended period of time and a wide range of temperature.

The development of more energetic solid-state batteries focused on the use of lithium-ion conducting materials with lithium anodes. Lithium iodide is the

most conductive of the alkali metal halides,  $10^{-7}$  S/cm at ambient temperature. Liang (6) discovered the addition of a dispersed phase, such as Al<sub>2</sub>O<sub>3</sub>, increased the conductivity by about 2 orders of magnitude. Liang and colleagues developed a commercial lithium solid state battery using various polyvalent metal salts as the cathode. The internal resistance of the cell was reduced by fabricating the electrolyte as a very thin layer, but the cells were limited to fairly modest current drains. The cells did exhibit excellent storage life at high temperatures such as 100°C.

The development of the in-situ electrolyte battery based upon the use of a lithium anode with an iodine-complex cathode resulted in a cell that found widespread use in cardiac pacemakers. These cells are fabricated by contacting the anode with the cathode so that the electrolyte LiI forms in-situ as a very thin layer.

Other techniques for obtaining more conducting electrolyte elements in solid-state cells have included the development of both glass and polymeric electrolytes. Solid electrolyte batteries for ambient temperatures have evolved through the following stages,

1. Crystalline ionic solid electrolytes - (AgI)
2. Double salts - (RbAg<sub>4</sub>I<sub>5</sub>)
3. Dispersed phase electrolytes - (LiI-Al<sub>2</sub>O<sub>3</sub>)
4. Ceramic compounds - (Na<sup>+</sup>-Al<sub>2</sub>O<sub>3</sub>)
5. In-situ formed electrolyte - (LiI)
6. Glass electrolytes - (LiI-Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub>)
7. Polymer electrolytes - (PEOG-LiClO<sub>4</sub>)

Little commercialization has occurred, but in the specialty areas the solid state batteries may be quite useful for highly stable, long-life, low power applications.

TABLE 1

Early Solid Electrolyte Battery Systems (3,4)

Systems	Cell potential (volts)
Ag/AgI/V <sub>2</sub> O <sub>5</sub>	0.46
Ag/AgBr/CuBr <sub>2</sub>	0.74
Ag/AgBr-Te/CuBr <sub>2</sub>	0.80
Ag/AgCl/KICl <sub>4</sub>	1.04
Ni-Cr/SnSO <sub>4</sub> /PbO <sub>2</sub>	1.2-1.5

### Acknowledgement

This work was supported in part by the Office of Naval Research.

### References

1. Foley, R.T., J. Electrochem. Soc. **116**, 161 (1969).
2. Owens, B.B., "Solid Electrolyte Batteries," Vol. 8, *Advances in Electrochemistry and Electrochemical Engineering* (P. Delahay and C. Tobias, eds.) J. Wiley, New York (1971).
3. Mrgudich, J.N., in the *Encyclopedia of Electrochemistry*, edited by C.A. Hampel, Reinhold Publishing Corp., New York, p. 84, (1964).
4. Shapiro, S.J., "Solid Electrolyte Batteries," Proc. 11th Annual Power Sources Conf., May 22-23, 1957 p. 3.
5. Owens, B.B., Patel, B.K., Skarstad, P.M. and Warburton, D.L., *Solid State Ionics*, **9** and **10** (1983).
6. Liang, C.C., J. Electrochem. Soc. **120**, 1289 (1973).

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

Accession For	
DTIC GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Avail and/or	
Dist	
A-1	

END

3-87

DTHIC